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Space Electrochemical Research and Technology Abstracts

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*Abstracts from proceedings of a conference held at
NASA Lewis Research Center
Cleveland, Ohio
May 1-3, 1995*

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National Aeronautics and
Space Administration

Office of Management

**Scientific and Technical
Information Program**

1995

AGENDA

Fifth Space Electrochemical Research and Technology (SERT) Conference

ADVANCED SECONDARY BATTERIES

May 2, 1995

Chairs	Jeff Brewer, George C. Marshall Space Flight Center Tom Miller, NASA Lewis Research Center	
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9:20 a.m.	High Performance Nickel Electrodes for Space Power Applications Prosper K. Adanuvor, Auburn University	5
9:40 a.m.	MAGNUM® NiCd Advanced Nickel-Cadmium Battery Cells Darren Scoles, Eagle-Picher Industries, Inc.	7
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*Abstract not available at time of printing.

FUEL CELLS

May 3, 1995

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ADVANCED CONCEPTS

May 3, 1995

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2:00 p.m.	Development of Electrochemical Super Capacitors for EMA Applications J.A. Kosek, Giner, Inc.	39
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COMMERCIALIZATION—DUAL USE

May 3, 1995

3:15 p.m. Tom Maloney,* NYMA, Inc.47

*Abstract not available at time of printing.

ADVANCED SECONDARY BATTERIES

DEVELOPMENT OF A MICRO-FIBER NICKEL ELECTRODE FOR NICKEL-HYDROGEN CELL

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ABSTRACT

Development of a high specific energy nickel electrode is the main goal of the lightweight nickel electrode program at the NASA Lewis Research Center. The approach has been to improve the nickel electrode by continuing combined in-house and contract efforts to develop a more efficient and lighter weight electrode for the nickel-hydrogen cell. Small fiber diameter nickel plaques are used as conductive supports for the nickel hydroxide active material. These plaques are commercial products and have an advantage of increased surface area available for the deposition of active material. Initial tests include activation and capacity measurements at different discharge levels followed by half-cell cycle testing at 80 percent depth-of-discharge in a low-Earth-orbit regime. The electrodes that pass the initial tests are life cycle-tested in a boiler plate nickel-hydrogen cell before flightweight designs are built and tested.

High Performance Nickel Electrodes for Space Power Applications

Prosper K. Adanuvor, Johnnie A. Pearson, Brian Miller and Bruce Tatarchuk

Department of Chemical Engineering and the Space Power Institute

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NASA-LEWIS Research Center

Electrochemical Technology Branch

Cleveland, Ohio 44135

The specific energy density and the performance of nickel electrodes are generally limited by the electrode microstructure and the nature of the active material within the electrode matrix. Progress is being made in our laboratory in a collaborative effort with NASA-LEWIS Research Center to develop lighter weight, mechanically stable and highly efficient nickel electrodes for aerospace applications. Our approach is based on an electrode microstructure fabricated from a mixture of nickel fibers as small as $2\mu\text{m}$ diameter and cellulose fibers. Results will be presented to show the optimum conditions for impregnating this electrode microstructure with nickel hydroxide active material. Performance data in half-cell tests and cycle life data will also be presented. The flexibility of this electrode microstructure and the significant advantages it offers in terms of weight and performance will be demonstrated, in particular its ability to accept charge at high rates and to discharge at high rates.

MAGNUM® NiCd ADVANCED NICKEL-CADMIUM BATTERY CELLS

Darren Scoles
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Colorado Springs, Colorado

Abstract

The Power Systems Department of Eagle-Picher Industries, Inc., located in Colorado Springs, Colorado, has developed a long-life advanced Nickel-Cadmium battery cell for aerospace applications. This battery cell, known as the MAGNUM® NiCd cell, offers significant life expectancy increase over traditional NiCd battery cells. In addition, it offers significant cost reduction from the Super NiCd® battery cell (developed by Hughes Aircraft Company and manufactured by the Power Systems Department of Eagle-Picher Industries, Inc.).

History/Reasons

Concept

NSWC CRANE Test Data (Cycle Life and Trend Plots)

- 21 Ah Pack 6000A (GSFC/JPL)
- 10 Ah Packs 6122M and 6106M (GSFC)
- 50 Ah Packs 6522M and 6506M (GSFC)

Future Test Plans (also at NSWC CRANE)

- 21 Ah Packs (for GSFC)
- 21 Ah Packs (for LeRC/Battery Steering Committee)

BENDING PROPERTIES OF NICKEL ELECTRODES FOR NICKEL-HYDROGEN BATTERIES

Bradley Lerch
NASA Lewis Research Center
Cleveland, Ohio

Recent changes in manufacturing have resulted in nickel-hydrogen batteries which fail prematurely by electrical shorting. This is believed to be a result of a blistering problem in the nickel electrodes. This study investigates the bending properties of nickel electrodes in an attempt to correlate the bending properties with the propensity of the electrode to blister. Nickel electrodes from three different batches of material were tested in both the as-received and impregnated forms. Effects of specimen curvature and position within the electrode on the bending strength were studied and within electrode and batch-to-batch variation were addressed. Two color imaging techniques were employed which allowed differentiation of phases within the electrodes. These techniques aided in distinguishing the relative amounts of nickel hydroxide surface loading on each electrode, relating surface loading to bend strength. Bend strength was found to increase with the amount of surface loading.

ABSTRACT

Effect of KOH Concentration and Anions on the Performance of Ni-H₂ Battery Positive Plate

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and

Gopalakrishna M. Rao
NASA Goddard Space Flight Center
Greenbelt, Maryland

The capacity and voltage behavior of electrochemically impregnated sintered nickel positive plates was examined by galvanostatic charging and discharging in a flooded electrolyte cell. Three different concentrations of KOH (40%, 31%, and 26%) and 31% KOH containing dissolved nitrate, sulfate or silicate were investigated. The end of charge voltage at C/10 charge and at 10°C showed the following order: 40% KOH > 31% KOH alone and in the presence of the anions > 26% KOH. The middischarge voltage at C/2 discharge was higher in 26% KOH, almost the same for 31% KOH with and without the added contaminants and much lower for 40% KOH. The plate capacity was marginally affected by cycling in all cases except for 40% KOH where the capacity declined after 1000 cycles at 80% DOD. At the end of cycling the plate tested in the presence of sulfate and silicate experienced measurable weight loss as a result of active material extrusion. Cyclic voltammetry of miniature electrodes in 31% KOH showed that the second oxidation peak that corresponds to the formation of a different phase of oxidized Ni has a lower peak current at -5°C compared to 25°C and oxygen evolution occurs at a higher potential at -5°C. The reduction peak (discharge reaction) is more polarized at 25°C compared to -5°C. The presence of silicate alters the potentials only marginally. The implications of these results in plate treatment and low temperature operation are discussed.

**Advanced Dependent Pressure Vessel (DPV)
Nickel-Hydrogen Spacecraft Cell and Battery Design**

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The dependent pressure vessel (DPV) nickel-hydrogen (NiH_2) battery is being developed as a potential spacecraft battery design for both military and commercial satellites. Individual pressure vessel (IPV) NiH_2 batteries are currently flying on more than 70 earth-orbital satellites and have accumulated more than 140,000,000 cell-hours in actual spacecraft operation. The limitations of standard NiH_2 IPV flight battery technology are primarily related to the internal cell design and the battery packaging issues associated with grouping multiple cylindrical cells. The DPV cell design offers higher specific energy and reduced cost, while retaining the established IPV NiH_2 technology flight heritage and database. The advanced cell design offers a more efficient mechanical, electrical and thermal cell configuration and a reduced parts count. The internal electrode stack is a prismatic flat-plate arrangement. The flat individual cell pressure vessel provides a maximum direct thermal path for removing heat from the electrode stack. The DPV cell geometry also minimizes multiple-cell battery packaging constraints by using an established end-plate/tie-rod battery design. A major design advantage is that the battery support structure is efficiently required to restrain only the force applied to a portion of the end cell. As the cells are stacked in series to achieve the desired system voltage, this increment of the total battery weight becomes small. The geometry of the DPV cell promotes compact, minimum volume packaging and places all cell terminals along the length of the battery. The resulting ability to minimize intercell wiring offers additional design simplicity and significant weight savings. The DPV battery design offers significant cost and weight savings advantages while providing minimal design risks. Cell and battery level design issues will be addressed including mechanical, electrical and thermal design aspects. A design performance analysis will be presented at both the cell and battery level. The DPV is capable of delivering up to 76 Watt-hours per kilogram (Wh/kg) at the cell level and 70 Wh/kg at the full battery level. This represents a 40% increase in specific energy at the cell level and a 60% increase in specific energy at the battery level compared to current IPV NiH_2 technology.

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Abstract not available at time of printing.

ELECTROLYTE MANAGEMENT CONSIDERATIONS IN MODERN
NICKEL HYDROGEN AND NICKEL CADMIUM CELL AND BATTERY DESIGNS
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THE AEROSPACE CORPORATION

In the early 1980s the NASA Lewis group addressed the topic of designing nickel hydrogen cells for LEO applications. As published in 1984, the design addressed the topics of gas management, liquid management, plate expansion, and the recombination of oxygen during overcharge. This design effort followed principles set forth in an earlier Lewis paper that addressed the topic of pore size engineering. At about that same time, the beneficial effect on cycle life of lower electrolyte concentrations was verified by Hughes Aircraft as part of a Lewis funded study. A succession of life cycle tests of these concepts have been carried out that essentially verified all of this earlier work.

During these past two decades, some of the mysteries involved in the active material of the nickel electrode have been resolved by careful research efforts carried out at several laboratories. At The Aerospace Corporation, Dr. Zimmerman has been developing a sophisticated model of an operating nickel hydrogen cell which will be used to model certain mechanisms that have contributed to premature failures in nickel hydrogen and nickel cadmium cells.

During the course of trying to understand and model abnormal nickel hydrogen cell behaviors, we have noted that not enough attention has been paid to the potassium ion content in these cells, and more recently batteries. Several of these phenomenon have been well known in the area of alkaline fuel cells, but only recently have they been examined as they might impact alkaline cell designs. This paper will review three general areas where the potassium ion content can impact the performance and life of nickel hydrogen and nickel cadmium devices. Once these phenomenon are understood conceptually, the impact of potassium content on a potential cell design can be evaluated with the aid an accurate model of an operating cell or battery. All three of these areas are directly related to the volume tolerance and pore size engineering aspects of the components used in the cell or battery design.

1. The gamma phase uptake of potassium ion can result in a lowering of the electrolyte concentration. This leads to a higher electrolyte resistance as well as electrolyte diffusional limitations on the discharge rate. This phenomenon will also impact the response of the cell to a reconditioning cycle.

2. The impact of low level shunt currents in multi-cell configurations will result in the movement of potassium ion from one part of the battery to another. This will impact the electrolyte volume/vapor pressure relationships within the cell or battery.

3. The transport of water vapor from place to place under the driving force of a temperature gradient has already impacted cells for the case where water vapor is condensed on a colder cell wall. The paper will explore the convective and diffusive movement of gases saturated with water vapor from a warmer plate pack to a cooler one - both with and without liquid communication.

FUEL CELLS

A NOVEL UNITIZED REGENERATIVE PROTON EXCHANGE MEMBRANE FUEL CELL

O.J. Murphy, A.J. Cisar, A. Gonzalez-Martin, C.E. Salinas and S.F. Simpson

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A difficulty encountered in designing a unitized regenerative proton exchange membrane (PEM) fuel cell lies in the incompatibility of electrode structures and electrocatalyst materials optimized for either of the two functions (fuel cell or electrolyzer) with the needs of the other function. This difficulty is compounded in previous regenerative fuel cell designs by the fact that water, which is needed for proton conduction in the PEM during both modes of operation, is the reactant supplied to the anode in the electrolyzer mode of operation and the product formed at the cathode in the fuel cell mode. Drawbacks associated with existing regenerative fuel cells have been addressed in work performed at Lynntech. In a first innovation, electrodes function either as oxidation electrodes (hydrogen ionization or oxygen evolution) or as reduction electrodes (oxygen reduction or hydrogen evolution) in the fuel cell and electrolyzer modes, respectively. Control of liquid water within the regenerative fuel cell has been brought about by a second innovation. A novel PEM has been developed with internal channels that permit the direct access of water along the length of the membrane. Lateral diffusion of water along the polymer chains of the PEM provides the water needed at electrode/PEM interfaces. Fabrication of the novel unitized regenerative fuel cell and results obtained on testing it will be presented.

FUEL CELL SYSTEMS FOR FIRST LUNAR OUTPOST – REACTANT STORAGE OPTION

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ABSTRACT

The office of Space, DOE, appointed a Lunar Surface Power Working Group to review candidate systems for the First Lunar Outpost habitat. The working group met for a total of five days in the fall of 1992 and concluded that the candidate involving a photovoltaic unit, a fuel cell, a regenerator to recycle the reactants, and storage of oxygen and hydrogen gases was the most attractive for this application. Most of the volume (97%) and weight (63%) are taken up by the reactants and their storage tanks. Therefore, in my work for the Group, and in this report, I have concentrated on finding ways to reduce these volumes and weights. Three options were considered: 1) the baseline case considered in the preliminary system design, that of separate high pressure (200 bar) storage tanks, 2) the use of two of the descent storage propellant tanks wrapped with graphite fibers to increase the pressure capability, and 3) the use of cryogenic storage of reactants in the propellant tanks. The first option results in high storage tank mass and volume. The second option saves 90% of the volume by making use of the propellant tanks, but it has little if any weight advantages; the weight saved by not providing extra tanks for reactant storage is nearly entirely added back by the weight of the additional material (graphite fibers) to strengthen the propellant tanks. Use of the descent storage propellant tanks for storage of the fuel cell reactants as cryogenic liquids requires a gas liquification system. The weight of this system is expected to be less than that of the storage tanks but it would require development and testing to prove its reliability. The solar array would have to be 40% larger and the heat projection range would be 170% larger than for storage of reactants as high pressure gases. For a high power system (>20 kW) the larger energy storage requirement would probably favor the cryogenic storage option.

ACKNOWLEDGEMENT

Work supported by the U. S. Department of Energy, Electrochemical Technology Program under Contract W-31-109-Eng-38.

Presenter: Dr. Thomas L. Cable
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Title: The TMI Regenerable Solid Oxide Fuel Cell

ABSTRACT

Energy storage and production in space requires rugged, reliable hardware which minimizes weight, volume, and maintenance while maximizing power output and usable energy storage. These systems generally consist of photovoltaic solar arrays which operate during sunlight cycles to provide system power and regenerate fuel (hydrogen) via water electrolysis; during dark cycles, hydrogen is converted by the fuel cell into system. The currently preferred configuration uses two separate systems (fuel cell and electrolyzer) in conjunction with photovoltaic cells. Fuel cell/electrolyzer system simplicity, reliability, and power-to-weight and power-to-volume ratios could be greatly improved if both power production (fuel cell) and power storage (electrolysis) functions can be integrated into a single unit.

The Technology Management, Inc. (TMI), solid oxide fuel cell-based system offers the opportunity to both integrate fuel cell and electrolyzer functions into one unit and potentially simplify system requirements. Based on the TMI solid oxide fuel cell (SOFC) technology, the TMI integrated fuel cell/electrolyzer utilizes innovative gas storage and operational concepts and operates like a rechargeable "hydrogen-oxygen battery."

Preliminary research has been completed on improved H_2/H_2O electrode (SOFC anode/electrolyzer cathode) materials for solid oxide, regenerative fuel cells. Improved H_2/H_2O electrode materials showed improved cell performance in both fuel cell and electrolysis modes in reversible cell tests. In reversible fuel cell/electrolyzer mode, regenerative fuel cell efficiencies (ratio of power out [fuel cell mode] to power in [electrolyzer mode]) improved from 50% (using conventional electrode materials) to over 80%. The new materials will allow the TMI SOFC system to operate as both the electrolyzer and fuel cell in a single unit.

Preliminary system designs have also been developed which indicate the technical feasibility of using the TMI SOFC technology for space applications with high energy storage efficiencies and high specific energy. Development of small space systems would also have potential dual-use, terrestrial applications.

Engineering Development Program of a Closed Aluminum-Oxygen Semi-cell System for an Unmanned Underwater Vehicle-An Update

Dane W. Gregg and Susan E. Hall

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ABSTRACT

Most emerging unmanned undersea vehicle (UUV) missions require significantly longer range and endurance than is achievable with existing battery technology. The Aluminum-Oxygen (Al-O₂) semi-cell is a candidate technology capable of providing a significant improvement in endurance compared to the silver-zinc battery technology currently used in UUVs and compares favorably to other proposed UUV power systems not only in performance, but also in safety and logistics. An Al-O₂ semi-cell system is under development by Loral Defense Systems-Akron (Loral) for the ARPA/Navy 44" diameter UUV test vehicle. The power plant consists of a cell stack, gas management, oxygen storage, electrolyte management, coolant and controller subsystems, designed to replace the existing silver-zinc battery and meet existing weight, volume, electrical and thermal requirements, therefore minimizing modifications to the UUV. A detailed system design is complete. A component and material endurance test to evaluate compatibility and reliability of various material and components is complete. Sub-scale (Short stack) system testing is complete. A full-scale demonstration unit is now under construction in the second half of 1995. The full scale demonstration test will simulate environmental conditions of the operational system. This paper summarizes the results of the extensive short stack and endurance test programs, describes the plan for full-scale testing, and concludes with a brief discussions of future directions for this technology. This program is sponsored by ARPA Maritime Systems Technology Office under NASA contract NAS3-26715.

Robert Savinell
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Cleveland, Ohio

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ADVANCED CONCEPTS

SPE®OBOGS: ON-BOARD OXYGEN GENERATING SYSTEM
J. McElroy and W. Smith

UNITED TECHNOLOGIES CORPORATION
Hamilton Standard Division
Windsor Locks, Connecticut

ABSTRACT

Regulations require oxygen usage by commercial airline flight crews during check out and during certain aircraft configurations. This oxygen is drawn from a high pressure on-board pressure cylinder storage system. In a typical aircraft, oxygen cylinder removal for oxygen ground servicing is conducted every 4 to 6 weeks.

An on-board oxygen generating system has been developed to eliminate the need for oxygen ground servicing. The SPE-OBOGS supplies oxygen during flight in a "trickle charge" mode to replenish the consumed oxygen at pressures up to 1850 psi.

The Electrochemical cell stack is the fundamental SPE-OBOGS system component. The same basic proton exchange membrane technology, previously used for the Gemini Program fuel cells and currently used in nuclear submarines as oxygen generators, is used in the SPE-OBOGS.

An in-service evaluation of the SPE-OBOGS is in the planning stage and a zero gravity version is being promoted for on orbit space suit oxygen system recharge.

Summary results of the SPE-OBOGS development will be addressed.

Abstract

Hermetically Sealed Aluminum Electrolytic Capacitor

by

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and

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Aluminum electrolytic capacitors are presently not allowed on NASA missions because they outgas water and organic vapors, as well as H_2 . As a consequence, much larger and heavier packages of tantalum capacitors are used. A hermetically sealed aluminum capacitor has been developed under NASA-MSFC SBIR contracts. This contains a nongassing electrolyte that was developed for this application so internal pressure would remain low. Capacitors rated at 250 to 540 V have been operated under full load for thousands of hours at 85° and 105°C with good electrical performance and low internal pressure. Electrolyte chemistry and seal engineering concepts will be discussed.

Fabrication of Advanced Electrochemical Energy Materials Using Sol-Gel Processing Techniques

C.T. Chu, Jay Chu, and Haixing Zheng
Chemat Technology, Inc., Northridge, CA 91324

Abstract

Advanced materials play an important role in electrochemical energy devices such as batteries, fuel cells, and electrochemical capacitors. They are being used as both electrodes and electrolytes. Sol-gel processing is a versatile solution technique used in fabrication of ceramic materials with tailored stoichiometry, microstructure, and properties. The application of sol-gel processing in the fabrication of advanced electrochemical energy materials will be presented. The potentials of sol-gel derived materials for electrochemical energy applications will be discussed along with some examples of successful applications. Sol-gel derived metal oxide electrode materials such as V_2O_5 cathodes have been demonstrated in solid-state thin film batteries; solid electrolytes materials such as β "-alumina for advanced secondary batteries had been prepared by the sol-gel technique long time ago; and high surface area transition metal compounds for capacitive energy storage applications can also be synthesized with this method.

Development of Electrochemical Super Capacitors for EMA Applications

J.A. Kosek, T. Dunning and A.B. LaConti

Giner, Inc., 14 Spring Street, Waltham, MA 02154-4497

In a NASA SBIR Phase I program (*Contract No. NAS8-40119*), Giner, Inc. evaluated the feasibility of fabricating an all-solid-ionomer multicell electrochemical capacitor having a unit cell capacitance greater than 2 F/cm^2 and a repeating element thickness of 6 mils. This capacitor can possibly be used by NASA as a high-rate energy source for electromechanical actuator (EMA) activation for advanced space missions. The high unit cell capacitance and low repeating element thickness will allow for the fabrication of a low-volume, low-weight device, favorable characteristics for space applications. These same characteristics also make the capacitor attractive for terrestrial applications, such as load-leveling batteries or fuel cells in electric vehicle applications.

Although the projected energy densities for electrochemical capacitors are about two orders of magnitude lower than that of batteries, the high-power-density characteristics of these devices render them as potentially viable candidates for meeting pulse or peak electrical power requirements for some anticipated aerospace mission scenarios, especially those with discharge times on the millisecond to second time scale. On a volumetric or gravimetric basis, the advantages of utilizing electrochemical capacitors rather than batteries for meeting the peak power demands associated with a specific mission scenario will largely depend upon the total and pulse durations of the power peaks.

The effect of preparation conditions on RuO_x , the active component in an all-solid-ionomer electrochemical capacitor, was evaluated during this program. Methods were identified to prepare RuO_x having a surface area $> 180 \text{ m}^2/\text{g}$, and a capacitance of $> 2 \text{ F/cm}^2$. Further efforts to reproducibly obtain these high-surface-area materials in scaled-up batches will be evaluated in Phase II. During this Phase I program we identified a superior Nafion 105 membrane, having a film thickness of 5 mils, that showed excellent performance in our all-solid ionomer capacitors and resulted in electrochemical capacitors with a repeating element thickness of 8 mils. We are currently working with membrane manufacturers to obtain a high-performance membrane in less than 3 mil thickness to obtain a repeating element thickness of 6 mils or less.

A 10-cell all-solid ionomer capacitor stack, with each cell having a 222 cm^2 active area, was fabricated and evaluated as part of the Phase I program. Further Scale-up of a high-energy-density stack is planned in Phase II.

High Energy Density Electrolytic Capacitor

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Recently a new type of electrolytic capacitor was developed. This capacitor, the Evans Hybrid combines an electrolytic capacitor anode with an electrochemical capacitor cathode. The resulting capacitor has four times the energy density of other electrolytic capacitors, with comparable electrical performance.

The prototype, a 480 μ F, 200 V device, had an energy density exceeding 4 J/cc. Now, a 680 μ F, 50 V, MIL-style all tantalum device has been constructed and is undergoing qualification testing. Pending a favorable outcome, work will begin on other ratings.

Potential for commercially significant development exists in applying this technology to aluminum-based electrolytic capacitors. It is possible to at least double the energy density of aluminum electrolytics, while using existing manufacturing methods, and without adding material expense.

Data presented include electrical characteristics and performance measurements of the 200 V and 50 V Hybrid capacitors and results of ongoing qualification status of the MIL-style tantalum.

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Abstract not available at time of printing.

COMMERCIALIZATION—DUAL USE

Tom Maloney
NYMA, Inc.
Brook Park, Ohio

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